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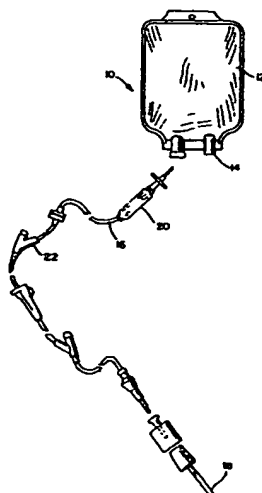
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(54) Title: CYCLOOLEFIN BLENDS AND METHOD FOR SOLVENT BONDING POLYOLEFINS



(57) Abstract: The present invention provides a polymer composition having a first component obtained by copolymerizing a norbornene monomer and an ethylene monomer, the first component being in an amount from about 1-99 % by weight of the composition; and a second component of an ethylene and α -olefin copolymer, the α -olefin having 6 carbons, the second component being in an amount from about 99 % to about 1 % by weight of the composition.

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Description

CYCLOOLEFIN BLENDS AND METHOD FOR SOLVENT BONDING POLYOLEFINS

Technical Field

This invention relates to polymer blends and more particularly to cyclic olefin containing polymers or bridged polycyclic hydrocarbon containing polymers blended with ethylene and α -olefin copolymers that are obtained utilizing a metallocene catalyst system.

Background Art

In the medical field, where beneficial agents are collected, processed and stored in containers, transported and ultimately delivered through drip chambers, tube connectors and tubes by infusion to patients, there has been a recent trend toward developing materials useful for fabricating such containers, tubings and devices without the disadvantages of currently used materials such as polyvinyl chloride. These new materials must have a unique combination of properties to be used in fluid administration sets. Among these are the materials in most instances must be optically clear, environmentally compatible, have sufficient yield strength and flexibility for flexible products and sufficient rigidity for rigid products, have a low quantity of low molecular weight additives, be capable of being solvent bonded to soft polyolefin medical products and be compatible with medical solutions.

It is desirable for medical products in an infusion delivery set to be optically transparent to allow for visual inspection of fluids therein.

It is also desirable that the medical materials be environmentally compatible as a great deal of medical products are disposed of in landfills and through incineration. Further benefits are realized by using a material which is thermoplastically recyclable.

For medical products that are disposed of by incineration, it is necessary to use a material that does not generate or minimizes the formation of by-products such as

inorganic acids which may be environmentally harmful, irritating, and corrosive. For example, PVC may generate objectionable amounts of hydrogen chloride (or hydrochloric acid when contacted with water) upon incineration, causing corrosion of the incinerator.

5 To be compatible with medical solutions, it is desirable that the components of the infusion delivery set be free from or have a minimal content of low molecular weight additives such as plasticizers, stabilizers and the like. In some applications, these components can be extracted into the therapeutic solutions that come into contact with the material. The additives may react with the therapeutic agents or otherwise render the
10 solution ineffective. This is especially troublesome in bio-tech drug formulations where the concentration of the drug is measured in parts per million (ppm), rather than in weight or volume percentages. Even minuscule losses of the bio-tech drug can render the formulation unusable. Because bio-tech formulations can cost several thousand dollars per dose, it is imperative that the dosage not be changed.

15 Polyvinyl chloride ("PVC") has been widely used to fabricate medical tubings and containers as it meets most of these requirements. However, because PVC by itself is a rigid polymer, low molecular weight components known as plasticizers must be added to render PVC flexible. These plasticizers may leach out of the medical product and into the fluid passing through the products to contaminate the fluid or to render the fluid
20 unusable. For this reason, and because of the difficulties encountered in incinerating PVC, there is a need to replace PVC in at least the fluid contacting portions of the infusion pathway and more preferably in its entirety.

 Polyolefins have been developed which meet many of the requirements of medical containers and tubing, without the disadvantages associated with PVC.
25 Polyolefins typically are compatible with medical applications because they have minimal extractability to the fluids and contents which they contact. Most polyolefins are environmentally sound as they do not generate harmful degradants upon incineration, and in most cases are capable of being thermoplastically recycled. Many polyolefins are cost effective materials that may provide an economic alternative to PVC. However,
30 there are many hurdles to overcome to replace all the favorable attributes of PVC with a polyolefin.

For example, because of the inert nature of polyolefins, due in part to the non-polar nature of the polymer, difficulties have been encountered in bonding the polyolefin materials to rigid housings positioned along the infusion pathway of an infusion set. Typically, medical containers such as I.V. bags are connected to a patient through a series
5 of connected tubing that have in fluid communication drip chambers, Y-type injection sites, venous catheters and the like between the bag and the patient. Many of these components include rigid housings manufactured from polycarbonates, acrylics, ABS, copolyesters and the like. The housings have sleeves in which the tubing is inserted in a telescoping fashion to attach the tube to the housing. Therefore, it is necessary for the
10 medical tubing to be connected to the rigid housing to form a fluid tight seal with the housings.

PVC tubing is typically secured within such housings using solvent bonding techniques. Solvent bonding requires exposing the end of the tubing to be inserted into the housing to a solvent such as cyclohexanone or methyl ethyl ketone. The solvent
15 effectively softens or dissolves the PVC so when the tubing is inserted into the housing, a bond is formed. Solvent bonding techniques, however, are ineffective on certain polyolefins including polyethylene and polypropylene. Problems have also been encountered in using adhesive bonding techniques.

European Patent Application No. 0 556 034 discloses a medical instrument of a
20 material containing a resin of a cyclic olefin compound or a bridged polycyclic hydrocarbon compound. The EP '034 Application discloses making devices such as syringes, injection needles, drip chambers, blood bags and tubing from these resins. While the EP '034 Patent application discloses a non-PVC material for fabricating medical products it does not disclose a method for bonding a rigid housing of a cyclic
25 olefin to a flexible tubing of a cyclic olefin or other polyolefins.

Cycloolefin blends are also well known for providing rigid, injection molded parts. For example, U.S. Patent No. 5,359,001 discloses a multiple component polymer blend having a first component of a cycloolefin, a second component of a polyolefin and a third component of a cycloolefin block copolymer to compatibilize the cycloolefin and
30 polyolefin. The '001 Patent discloses such blends for impact modifying the highly rigid

and brittle cycloolefins. The '001 Patent does not disclose a method for solvent bonding these blends.

United States Patent No. 5,863,986 discloses polymer alloy blends of a cycloolefin copolymers with one or more core-shell particles and one or more block
5 copolymers. Again, these polymer blends are tough on impact and have high flexural strength and elongation at break. The '986 patent does not disclose a method for solvent bonding the polymer alloy blends.

Disclosure of Invention

10 The present invention provides multiple component polymer blends for fabricating medical devices. The blends of the present invention contain as a component homopolymers or copolymers of cyclic olefins or bridged polycyclic hydrocarbons. For example, the present invention provides a polymer composition comprising: a first
15 component obtained by copolymerizing a norbornene monomer and an ethylene monomer, the first component being in an amount from about 1-99% by weight of the composition; and a second component of an ethylene and α -olefin copolymer, the α -olefin having 6 carbons, the second component being in an amount from about 99% to about 1% by weight of the composition. It has been found by the present inventors that
20 α -olefin having 6 carbons when blended with norbornene result in blends having greater clarity when compared with blends of norbornene with α -olefins having 4 or 8 carbons. In a preferred form of the invention the ethylene and α -olefin copolymer is obtained using a metallocene catalyst.

The present invention also provides three component polymer blends where a second homopolymer or copolymer of a cyclic olefin or a bridged polycyclic
25 hydrocarbon is added to the above-described two-component blend. In a preferred form of the invention, the norbornene has a glass transition temperature of lower than 120°C and the second homopolymer or copolymer of a cyclic olefin or a bridged polycyclic hydrocarbon has a glass transition temperature of higher than 120°C.

30 Brief Description of Drawings

Fig. 1 shows a diagrammatic view of an infusion delivery set; and

Fig. 2 shows a diagrammatic view of a syringe barrel having end closures solvent bonded thereto.

Best Mode for Carrying Out the Invention

5 While the invention is susceptible of embodiment in many different forms, there is shown in the drawings and will herein be described in detail preferred embodiments of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments illustrated.

10 Figure 1 shows an infusion delivery set 10 having an I.V. container 12 and port tube 14 connected to a tubing 16 which provides at its distal end a venous catheter 18 for establishing fluid-flow access to a vascular system of a patient. Positioned at intermediate portions of the infusion pathway is a drip chamber 20 and a Y-type injection site 22. It should be understood that other rigid medical housings include filter housings,
15 tubing unions and others well known in the art, and that these components could be used in any combination in a delivery set 10. Figure 2 shows a syringe barrel 24 having end closures 26 solvent bonded on opposite ends of the syringe barrel. Of course the end closure 26 can be on one or both ends of the syringe barrel 24.

As will be described below, the present invention provides polymers and
20 copolymers containing monomers of cyclic olefins (which sometimes shall be referred to as cyclic olefin containing polymers) and blends thereof as well as homopolymers and copolymers containing monomers of bridged polycyclic hydrocarbons (which sometimes shall be referred to as bridged polycyclic hydrocarbon containing polymers) and blends thereof to fabricate both the flexible, rigid and semi-rigid components of the delivery set
25 10 and further provides solvent bonding and cement bonding techniques for attaching together olefin components to fabricate medical device assemblies and subassemblies contained in an infusion set or other medical devices well known in the medical arts.

The term polyolefin used herein is meant to include homopolymers and copolymers of ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, and decene. Suitable copolymers of ethylene include: (a) ethylene copolymerized with
30 monomers selected from the group of α -olefins having 3-10 carbons, lower alkyl and

lower alkene substituted carboxylic acids and ester and anhydride derivatives thereof, (b) ethylene propylene rubbers, (c) EPDM, and (d) ionomers. Preferably, the carboxylic acids have from 3-10 carbons. Such carboxylic acids therefore include acetic acid, acrylic acid and butyric acid. The term "lower alkene" and "lower alkyl" is meant to include a carbon chain having from 3-18 carbons more preferably 3-10 and most preferably 3-8 carbons. Thus, a subset of this group of comonomers includes, as a representative but non-limiting example, vinyl acetates, vinyl acrylates, methyl acrylates, methyl methacrylates, acrylic acids, methacrylic acids, ethyl acrylates, and ethyl acrylic acids.

10

I. Cyclic Olefins and Bridged Polycyclic Hydrocarbons

Suitable homopolymer and copolymers of cyclic olefins and bridged polycyclic hydrocarbons and blends thereof can be found in U.S. Patent Nos. 5,218,049, 5,854,349, 5,863,986, 5,795,945, 5,792,824; EP 0 291,208, EP 0 283,164, EP 0 497,567 which are incorporated in their entirety herein by reference and made a part hereof. In a preferred form of the invention these homopolymers, copolymers and polymer blends will have a glass transition temperature of greater than 50°C, more preferably from about 70°C to about 180°C, a density greater than 0.910 g/cc and more preferably from 0.910g/cc to about 1.3 g/cc and most preferably from 0.980 g/cc to about 1.3 g/cc and have from at least about 20 mole % of a cyclic aliphatic or a bridged polycyclic in the backbone of the polymer more preferably from about 30-65 mole % and most preferably from about 30-60 mole %.

In a preferred form of the invention, suitable cyclic olefin monomers are monocyclic compounds having from 5 to about 10 carbons in the ring. The cyclic olefins can selected from the group consisting of substituted and unsubstituted cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene. Suitable substituents include lower alkyl, acrylate derivatives and the like.

In a preferred form of the invention, suitable bridged polycyclic hydrocarbon monomers have two or more rings and more preferably contain at least 7 carbons. The rings can be substituted or unsubstituted. Suitable substitutes include lower alkyl, aryl,

aralkyl, vinyl, allyloxy, (meth) acryloxy and the like. The bridged polycyclic hydrocarbons are selected from the group consisting of those disclosed in the above incorporated patents and patent applications. Suitable bridged polycyclic hydrocarbon containing polymers are sold by Ticona under the tradename TOPAS, by Nippon Zeon
5 under the tradename ZEONEX and ZEONOR, by Daikyo Gomu Seiko under the tradename CZ resin, and by Mitsui Petrochemical Company under the tradename APEL.

Suitable comonomers include α -olefins having from 3-10 carbons, aromatic hydrocarbons, other cyclic olefins and bridged polycyclic hydrocarbons.

It may also be desirable to have pendant groups associated with the above-
10 mentioned homopolymers and copolymers. The pendant groups are for compatibilizing the cyclic olefin containing polymers and the bridged polycyclic hydrocarbon containing polymers with more polar polymers including amine, amide, imide, ester, carboxylic acid and other polar functional groups. Suitable pendant groups include aromatic hydrocarbons, carbon dioxide, monoethylenically unsaturated hydrocarbons,
15 acrylonitriles, vinyl ethers, vinyl esters, vinylamides, vinyl ketones, vinyl halides, epoxides, cyclic esters and cyclic ethers. The monethylenically unsaturated hydrocarbons include alkyl acrylates, and aryl acrylates. The cyclic ester includes maleic anhydride.

II. Blends Containing Cyclic Olefin Containing Polymers and/or Bridged Polycyclic Hydrocarbon Containing Polymers

20 Suitable two-component blends of the present invention include as a first component the homopolymers and copolymers of the cyclic olefin containing polymers and the bridged polycyclic hydrocarbon containing polymers (collectively hereinafter sometimes referred to as "COCs") described above in Section I. The COCs should be present in an amount from about 1-99% by weight of the blend, more preferably from
25 about 30-99%, and most preferably from about 35-99 weight percent or any combination or subcombination or ranges therein. In a preferred form of the invention the first components has a glass transition temperature of from about 70°C to about 130°C and more preferably from about 70-110°C.

The blends further include a second component in an amount by weight of the
30 blend of from about 99-1%, more preferably from about 70-1% and most preferably from about 65-1%. The second component is selected from the group consisting of

homopolymers and copolymers of ethylene, propylene, butene, hexene, octene, nonene, decene and styrene. The second component preferably has a density of from about 0.870-0.960 g/cc and more preferably from about 0.910-0.960 g/cc and more preferably from about 0.930-0.960 g/cc. In a preferred form of the invention the second component is and
5 ethylene and α -olefin copolymer where the α -olefin has from 3-10 carbons, more preferably from 4-8 carbons and most preferably 6 carbons. Most preferably the ethylene and α -olefin copolymers are obtained using a metallocene catalyst.

Suitable three-component blends include as a third component a COC selected from those COCs described in Part I above and different from the first component. In a
10 preferred form of the invention the second COC will have a glass transition temperature of higher than about 120°C when the first COC has a glass transition lower than about 120°C. In a preferred form of the invention, the third component is present in an amount by weight of from about 10-90% by weight of the blend and the first and second components should be present in a ratio of from about 2:1 to about 1:2 respectively of the
15 first component to the second component.

In a preferred form of the invention, random and block copolymers of norbornene and ethylene are selected as the first component of the blend. These norbornene copolymers are described in detail in U.S. Patent Nos. 5,783,273, 5,744,664, 5,854,349, and 5,863,986. The norbornene ethylene copolymer preferably has from at least about 20
20 mole percent norbornene monomer and more preferably from about 20-75 mole percent and most preferably from about 30-60 mole percent norbornene monomer or any combination or subcombination of ranges therein. The norbornene ethylene copolymer should have a glass transition temperature of from about 70-180°C, more preferably from 70-130°C and even more preferably from about 70-100°C.

25 The second component is preferably an ethylene copolymerized with an α -olefin having 6 carbons. It has been found by the present inventors that using this ethylene and a 6 carbon α -olefin as the second component yields blends with higher clarity when compared to blends having ethylene copolymerized with α -olefins having 4 or 8 carbons. Preferably, the ethylene and α -olefin copolymers are obtained using metallocene
30 catalysts. Suitable catalyst systems, among others, are those disclosed in U.S. Patent Nos. 5,783,638 and 5,272,236. Suitable ethylene and α -olefin copolymers include those

sold by Dow Chemical Company under the AFFINITY and ENGAGE tradenames, those sold by Exxon under the EXACT tradename and those sold by Phillips Chemical Company under the tradename MARLEX.

As set forth above, the first component of the norbornene/ethylene copolymer can
5 be present from about 1-99% by weight of the blend, more preferably from about 30-99% by weight, and most preferably 35-99% by weight.

In a preferred three-component blend a second norbornene and ethylene copolymer is added to the two component norbornene-ethylene/ethylene 6 carbon α -olefin blend. The second norbornene ethylene copolymer should have a norbornene
10 monomer content of 30 mole percent or greater and more preferably from about 35-75 mole percent and a glass transition temperature of higher than 120°C when the first component has a glass transition temperature of lower than 120°C.

III. Medical Products

15 Medical devices such as those shown in Figure 1 may be fabricated from the COCs set forth above. The present invention provides for fabricating, rigid, semi-rigid and flexible devices from the COCs. What is meant by the use of the term "rigid" herein is parts having a modulus of elasticity of at least 150,000 psi when measured in accordance with ASTM D790. What is meant by the term "semi-rigid" is parts having
20 a modulus of elasticity of greater than 20,000 psi but less than 150,000 psi when measured in accordance with ASTM D790. What is meant by the term "flexible" is articles having a modulus of elasticity of less than about 20,000 psi when measured in accordance with ASTM D790.

Rigid parts such as Y-sites, filter housings, injection sites, spikes, syringe barrels,
25 closures and others may be fabricated from the COCs by injection molding, blow molding, thermoforming processes or other plastic fabricating techniques. Semi-rigid parts such as drip chambers and closures may be fabricated from injection molding, blow molding, thermoforming and extrusion processes. Flexible parts such as medical tubing, closures and medical containers may be obtained using extrusion, coextrusion,
30 lamination, blow molding and injection molding processes.

For flexible and semi-rigid components such as tubing, containers and drip chamber 20, suitable polymers also include other polyolefins such as ethylene vinyl acetate copolymers having a vinyl acetate content of from about 5% to about 32%, ethylene methacrylate copolymers, ethylene and α -olefin copolymers having a density of less than 0.910 g/cc, flexible polypropylenes such as Huntsman's REFLEX and Montell's ADFLEX and stereo block homopolymers of polypropylene disclosed in U.S. Patent No. 5,594,080. Suitable polymers also include polymer blends and films such as those disclosed in U.S. Patent No. 5,849,843 and U.S. Patent Application Serial No. 08/153,602.

10 IV. Method of Solvent Bonding COCs

The present invention provides a method for assembling components of an infusion set into medical assemblies using solvent bonding techniques. Solvent bonding techniques can be used to join together any combination of rigid, semi-rigid and flexible parts including joining two rigid components, a rigid component to a semi-rigid component, a rigid component to a flexible component, a semi-rigid component to a flexible component, a semi-rigid component to another semi-rigid component, and certain flexible components to one another.

The method of solvent bonding includes the steps of: (1) providing a first article of a polymer composition described above in Sections I and II such as those having a first component of cyclic olefin containing polymer or a bridged polycyclic hydrocarbon containing polymer, the first component being present in an amount from about 30% to about 100% by weight of the composition; (2) providing a second article of a material selected from the group comprising low crystallinity polymers; (3) applying a solvent to one of the first article or the second article to define an interface area; and (4) bonding the first article to the second article along the interface area. Suitable low crystallinity polymers to fabricate the second article include COCs, COC blends having minimally 30% COC by weight, polymethyl pentene, polyolefins having a modulus of elasticity of less than 10,000 psi when measured in accordance with ASTM D790, and styrene containing polymers without modulus limitations.

30 Suitable solvents are those having a solubility parameter of less than about 20 (MPa)^{1/2}, more preferably less than about 19 (MPa)^{1/2} and most preferably less than about

18 (MPa)^{1/2} and include, but are not limited to, aliphatic hydrocarbons, aromatic hydrocarbons, mixtures of aliphatic hydrocarbons, mixtures of aromatic hydrocarbons and mixtures of aromatic and aliphatic hydrocarbons. Suitable aliphatic hydrocarbons include substituted and unsubstituted hexane, heptane, cyclohexane, cycloheptane, 5 decalin, and the like. Suitable aromatic hydrocarbons include substituted and unsubstituted aromatic hydrocarbon solvents such as xylene, tetralin, toluene, and cumene. Suitable hydrocarbon substituents include aliphatic substituents having from 1-12 carbons and include propyl, ethyl, butyl, hexyl, tertiary butyl, isobutyl and combinations of the same. What is meant by the terms "aliphatic hydrocarbon" and 10 "aromatic hydrocarbon" is a compound containing only carbon and hydrogen atoms. Suitable solvents will also have a molecular weight less than about 200 g/mole, more preferably less than about 180 g/mole and most preferably less than about 140 g/mole.

The first article can be rigid, semi-rigid and flexible medical product selected from the group consisting of Y-sites, filter housings, drip chambers, heparin locks, 15 injection sites, catheters, spikes, syringe barrels, closures, tubings, oxygenators, pump cassettes, valves, burretes, and any medical article or component. The second article can be rigid, semi-rigid and flexible polymeric material selected from the group comprising polyolefins, styrene containing polymers, cyclic olefin containing polymers and bridged polycyclic hydrocarbon containing polymers. The second article can be of the same 20 device set forth for the first article.

In a preferred form of the invention, the method comprises the steps of: (1) providing a first article of a polymer composition comprising: (a) a first component obtained by polymerizing a norbornene monomer and an ethylene monomer, the norbornene monomer being present in an amount of at least about 20 mole percent of the 25 copolymer, the first component being present in an amount from about 30% to about 100% by weight of the composition; and (b) a second component of a first ethylene and α -olefin copolymer, the second component being in an amount from about 70% to about 0% by weight of the composition; (2) providing a second article of low crystallinity polymers; (3) applying a solvent to one of the first article or the second article to define 30 an interface area; and (4) bonding the first article to the second article along the interface area.

V. COC Cement

For those flexible polymers that do not bond well to other flexible polymers using the solvent bonding techniques described above in Section IV, the present invention provides a cyclic olefin containing polymer based cement composition or bridged polycyclic hydrocarbon containing polymer based cement composition. The first component of the cement composition is selected from those set forth in Section I above and include a homopolymer or copolymer of a cyclic olefin or a bridged polycyclic hydrocarbon in an amount from 1-20% by weight of the composition, more preferably from 1-15% and most preferably from 3-10%, and a second component of a solvent having a solubility parameter of less than about 20 (Mpa)^{1/2} more preferably less than about 19 (Mpa)^{1/2} and most preferably less than about 18 (Mpa)^{1/2} and more preferably selected from the group of aliphatic hydrocarbons and aromatic hydrocarbons set forth above in Section IV. Suitable solvents will also have a molecular weight less than about 200 g/mole, more preferably less than about 180 g/mole and most preferably less than about 140 g/mole.

These cement compositions can also be used for bonding flexible articles to rigid articles, flexible articles to semi-rigid articles, semi-rigid articles to one another or for bonding semi-rigid articles to rigid articles or for bonding rigid articles to one another. Accordingly, the cement compositions can be used to prepare medical device assemblies such as joining flexible tubings to one another, joining flexible tubings to tubing unions and flexible tubings to drip chambers, flexible tubings to Y-sites and other rigid housings or any of the components of the medical infusion set or other medical device assemblies.

It may also be desirable to include in the cement composition polymer resins from the articles being joined. These optional components can be added in an amount by weight of the composition from 0-10%, more preferably from 0.2-5% and most preferably from 0.2-3%. The third component can be selected from the group comprising polyethylene copolymers having a density less than 0.880 g/cc, polymethyl pentene, polypropylene having a modulus of less than 10,000 psi and more preferably less than 4,000 psi, and certain styrene containing copolymers and interpolymers. Typically these flexible type polypropylenes are atactic. Certain polypropylene copolymers with ethylene are also suitable. Suitable styrene containing polymers include Dow's

interpolymer of styrene sold under the tradename INDEX. Other suitable styrene containing polymers include SBS, SIS and hydrogenated derivatives thereof such as SEBS and SEPS.

The method of using a polymeric cement to assemble medical devices comprises the steps of: (1) providing a first article of a low crystallinity polymer set forth above; (2) providing a second article of a low crystallinity polymer set forth above; (3) providing a cement composition having a first component of a cyclic olefin containing polymer or a bridged polycyclic hydrocarbon containing polymer and a second component of an effective amount of a solvent having a solubility parameter of less than about 20 (MPa)^{1/2} and more preferably selected from the group of aliphatic hydrocarbons and aromatic hydrocarbons having a molecular weight less than about 200 g/mole; (4) applying the cement composition to one of the first and second articles to define a bonding area; and (5) attaching the first article to the second article along the bonding area to fixedly attach the first article to the second article.

Suitable polyolefins for the first and second articles can be selected from the group comprising homopolymers and copolymers of ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, and decene. Suitable copolymers of ethylene include: (a) ethylene copolymerized with monomers selected from the group of α -olefins having 3-10 carbons, lower alkyl and lower alkene substituted carboxylic acids and ester and anhydride derivatives thereof, (b) ethylene-propylene rubbers, (c) EPDM, and (d) ionomers. Preferably, the carboxylic acids have from 3-10 carbons. Such carboxylic acids therefore include acetic acid, acrylic acid and butyric acid. The term "lower alkene" and "lower alkyl" is meant to include a carbon chain having from 3-18 carbons more preferably 3-10 and most preferably 3-8 carbons. Thus, a subset of this group of comonomers includes, as a representative but non-limiting example, vinyl acetates, vinyl acrylates, methacrylates, methyl methacrylates, acrylic acids, methyl acrylic acids, ethyl acrylates, and ethyl acrylic acids.

The first component of the cement composition can also be a copolymer of the cyclic olefins or the bridged polycyclic hydrocarbons set forth above in Section I. Suitable comonomers of the COCs can be selected from the group comprising α -olefins having from 2-10 carbons, aromatic hydrocarbons, cyclic hydrocarbons, and bridged

polycyclic hydrocarbons. In a preferred form of the invention the first component is a copolymer of a norbornene monomer and an ethylene monomer and more preferably the norbornene monomer is present in at least about 20 mole percent of the copolymer and even more preferably the norbornene is present from about 30 to about 60 mole percent.

5 The cement composition can also have an additional optional component selected from the group of polyethylene copolymers having a density less than about 0.880 g/cc, polymethyl pentene, polypropylene having a modulus of less than about 10,000 psi and more preferably less than about 4,000 psi, and certain styrene containing copolymers and interpolymers. Typically these flexible type polypropylenes are atactic. Certain
10 polypropylene copolymers with ethylene are also suitable. Suitable styrene and ethylene containing polymers include Dow's interpolymer of styrene sold under the tradename INDEX. Other suitable styrene containing polymers include SBS, SIS and hydrogenated derivatives thereof such as SEBS and SEPS.

In a preferred form of the invention, the method for using a polymeric cement to
15 assemble medical devices comprises the steps of: (1) providing a first article of a low crystallinity polymer set forth above; (2) providing a second article of a low crystallinity polymer set forth above; (3) providing a cement composition comprising: (a) a first component in an amount by weight of from 1-20% of the cement composition and obtained by copolymerizing a norbornene monomer and an ethylene monomer, the
20 norbornene monomer being present in an amount of at least about 20 mole percent of the copolymer; (b) a second component of a solvent in an amount by weight from about 99% to about 80% of the cement composition; and (c) an optional third component in an amount by weight from about 0-10% by weight of the cement composition and selected from the group of optional components set forth above; (4) applying the cement
25 composition to one of the first and second articles to define a bonding area; and (5) attaching the first article to the second article along the bonding area to fixedly attach the first article to the second article.

The present invention also provides a medical device assembly. The assembly has a first article of a first polymeric material selected from the group comprising
30 polyolefins, styrene containing polymers, cyclic olefin containing polymers and bridged polycyclic hydrocarbon containing polymers. The assembly also has a second article of

a polymeric material selected from the group comprising polyolefins, styrene containing polymers, cyclic olefin containing polymers and bridged polycyclic hydrocarbon containing polymers. The first article is attached to the second article with a cement composition. The cement composition has a first component of a cyclic olefin containing polymer or a bridged polycyclic hydrocarbon containing polymer and an effective amount of a solvent having a solubility parameter of less than about 20 (MPa)^{1/2} and more preferably selected from the group of aliphatic hydrocarbons and aromatic hydrocarbons having a molecular weight less than about 200 g/mole. The following are non-limiting examples of the present invention.

10

Examples:

Example I. Test methods for resin properties:

Tensile Modulus: ASTM D638.

15

Flexural Modulus: ASTM D790.

Glass Transition Temperature: DSC.

Light Transmittance: ASTM D1003.

Example II. Resin Properties:

20

(1) COC Resins:

Topas resins are produced by Ticona, a member of the Hoechst Group.

CZ Resin is marketed by the Daikyo Gomu Seiko and The West Company.

Zeonex resin is produced by Nippon Zeon Co., Ltd.

25

Resin	Glass Transition Tg. (°C)	Tensile Modulus (kpsi)	Light Transmittance (%)
Topas 8007	85	377	92
Topas 6013	130	464	92
Topas 6015	160	464	92
Topas 6017	180	464	92
CZ Resin	140	341	91
Zeonex 280	140	341	91

30

35

(2) Non-COC Resins:

	Material	Tensile/Flexural Modulus (kpsi)	Density (g/cc)	Comonomer
5	<hr/>			
	Polyethylene:			
	Dow Chemicals Affinity VP8770	5	0.885	Octene
	Dow Chemicals Affinity PL1880	12	0.903	Octene
	Du Pont Dow Engage 8003	5	0.885	Octene
10	Du Pont Dow Engage 8411	3	0.880	Octene
	Dow Chemicals Dowlex 2045	38	0.920	Octene
	Mitsui Tafmer A4085	5	0.885	Butene
	Exxon Exact 3024	14	0.905	Butene
	Exxon Exact 3128	12	0.900	Butene
15	Exxon Exact 4033	3	0.880	Butene
	Exxon Exact 3030	14	0.905	Hexene
	Exxon Exact 3131	11	0.900	Hexene
	Phillips Marlex mPACT D143	23	0.916	Hexene
	Phillips Marlex mPACT D350	64	0.933	Hexene
20	Polypropylene:			
	Huntsman Rexflex W304	2	0.88	
	Huntsman Rexflex W210	4	0.89	
25	EVA			
	Du Pont Elvax CM576	2.5	0.95	
	Polybutene			
	Montell PB0200	35	0.915	
30	Montell PB8340	32	0.908	
	Styrenic copolymer			
	Phillips K-Resin KR03	210	1.01	
35	Shell Kraton G 1657	0.4	0.90	

(3) Solvents used in the examples:

All solvents were purchased from the Sigma-Aldrich Co.

The solubility parameters reported below are the Hansen Solubility Parameters at 25 degree C, as listed in the Polymer Handbook, 3rd Ed., Chapter VII, Pages 540-544 unless otherwise specified.

5

	Solvent	Solubility Parameter(MPa) ^{1/2}	Molecular Weight (g/mol)	Type of compound
10	Cyclohexane	16.8	84	Aliphatic hydrocarbon
	Methyl cyclohexane	16.0	98	Aliphatic hydrocarbon
	Ethyl cyclohexane	16.3*	112	Aliphatic hydrocarbon
	Propyl cyclohexane	16.2*	126	Aliphatic hydrocarbon
	n-Butyl cyclohexane	16.2*	140	Aliphatic hydrocarbon
	t-Butyl cyclohexane	--	140	Aliphatic hydrocarbon
15	Decalin	18.0-18.8	138	Aliphatic hydrocarbon
	Heptane	15.3	100	Aliphatic hydrocarbon
	Xylene	18.0	106	Aromatic hydrocarbon
	Tetralin	20.0	132	Aromatic hydrocarbon
	Cumene	17.6*	120	Aromatic hydrocarbon
	Toluene	18.2	92	Aromatic hydrocarbon
20	Cyclohexanone	19.6	98	Ketone
	Methyl ethyl ketone	19.0	72	Ketone
	Methylene chloride	20.3	85	Halohydrocarbon
	Tetrahydrofuran	19.4	72	Ether
	Dimethyl formamide	24.8	73	Nitrogen containing compound
	Dimethyl sulfoxide	26.6	78	Sulfur containing Compound

30 * Data from CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd Ed.

Example III. Test articles and solvent bonding test results:

35 All the COC blends set forth in the table below were prepared using a Brabender mixer, mixed at 250°C at 50 rpm for about 4 minutes, and then compression molded into 0.010" to 0.025" thick sheets at 450°F.

40	COC Blend Composition	Blend Ratio (wt %)	Material Rigidity	Strength of Solvent Bonding ⁽¹⁾		
				to ULDPE ⁽²⁾ (flexible)	to EVA ⁽³⁾ (flexible)	to COC ⁽³⁾ (rigid)
45	Topas 8007/Tafmer A4085	0/100	flexible	none	none	good
		30/70	semi-rigid	weak	weak	good
		50/50	rigid	good	good	strong
		70/30	rigid	strong	strong	strong

5	Topas 8007/Affinity VP8770	0/100	flexible	none	none	good
		50/50	rigid	good	good	strong
	Topas 8007/Affinity PL1880	0/100	flexible	none	none	weak
		50/50	rigid	good	good	strong
	Topas 8007/Engage 8411	0/100	flexible	none	none	good
		50/50	rigid	good	good	strong
10	Topas 8007/Exact 3024	0/100	flexible	none	none	weak
		50/50	rigid	good	good	strong
		70/30	rigid	strong	strong	strong
15	Topas 8007/Exact 3128	0/100	flexible	none	none	weak
		50/50	rigid	good	good	strong
20	Topas 8007/Exact 4033	0/100	flexible	none	none	good
		50/50	rigid	good	good	strong
	Topas 8007/Engage8003	30/70	semi-rigid	weak		
		40/60	rigid	good		
		50/50	rigid	good		
		60/40	rigid	strong		
70/30		rigid	strong			
25		80/20	rigid	strong		
		90/10	rigid	strong		
30	Topas 6017/Dowlex 2045	0/100	semi-rigid	none	none	none
		50/50	rigid	good	good	strong
	Topas 6015/Tafmer A4085	30/70	rigid	weak	weak	good
50/50		rigid	good	good	strong	
70/30		rigid	good	good	strong	
35	Topas 8007/Rexflex W304	0/100	flexible	none	none	good
		30/70	semi-rigid	weak	weak	good
		50/50	rigid	good	good	strong
		70/30	rigid	strong	strong	strong
40	Topas 8007/PB0200	0/100	semi-rigid	none	none	none
		50/50	rigid	good	good	strong

	Topas 8007/PB8340	0/100	semi-rigid	none	none	none
		50/50	rigid	good	good	strong
5	Topas 6015/PB0200	50/50	rigid	good	good	strong
	Topas 6015/PB8340	50/50	rigid	good	good	strong
10	Topas 8007/Kraton G1657	0/100	flexible	none	none	good
		30/70	semi-rigid	weak	weak	good
		50/50	rigid	good	good	strong
		70/30	rigid	good	good	strong
15	Topas 8007/K-Resin KR01	0/100	rigid	none	none	weak
		50/50	rigid	good	good	strong
	Topas 6015/K-Resin KR01	50/50	rigid	good	good	strong
20	Topas 6015/Tafmer A4085/KratonG1657					
		60/20/20	rigid	good	good	strong
25	Topas 6017/Topas 8007/Affinity VP8770					
		25/25/50	rigid	good	good	strong
		30/20/50	rigid	good	good	strong
	Topas 6015/Topas 8007/Affinity VP8770					
		25/25/50	rigid	good	good	strong

30 1) The solvent used is cyclohexane.

Bond strength was assessed by hand pull test, at one day after the solvent bonding.

Ratings:

None = Readily separable.

35 Weak = Some bond strength but easy to separate.

Good = Hard to separate, no material transfer is visible on the peeled surface but is suitable for providing a sterile, sturdy connection.

Strong = Very hard to separate, material transferring from one surface to another at the peeling bonding interface is visible.

40 2) The ULDPE specimen was made from Dow Chemicals Engage 8003 resin and was extruded into a tube.

3) The EVA specimen was made from DuPont Elvax CM576 resin which had 28% VA content, and was extruded into a tube.

4) The COC specimen was made from Topas 8007 resin and was injection molded into y-site with the bonding site in a tube geometry.

5

IV. Examples of using different solvents to bond COC containing devices:

10	Combination	Material-1 to Material-2	Solvent	Bond Strength
15	Rigid to Flexible	Topas8007 ^(a) to Engage 8003 ^(b)	Cyclohexane	good
			Ethyl cyclo hexane	good
			Propyl cyclo hexane	good
			n-Butyl cyclo hexane	good
			t-Butyl cyclo hexane	good
			Xylene	good
			Tetralin	good
			Decalin	good
			Heptane	good
			Cumene	good
			Toluene	weak
			Cyclohexanone	none
			Methyl ethyl ketone	none
			Methylene chloride	none
			Tetrahydrofuran	none
20	Rigid to Flexible	Topas8007 ^(a) to Engage 8003 ^(b)	Dimethyl formamide	none
			Dimethyl sulfoxide	none
25	Rigid to Flexible	Topas8007 ^(a) to Engage 8003 ^(b)		
30	Rigid to Flexible	Topas8007 ^(a) to Engage 8003 ^(b)		
35	Rigid to Flexible	Topas8007 ^(a) to Elvax CM576 ^(b)	Cyclohexane	good
			Ethyl cyclo hexane	good
			Propyl cyclo hexane	good
			n-Butyl cyclo hexane	good
			t-Butyl cyclo hexane	good
			Xylene	good
			Tetralin	good
			Decalin	good
			Heptane	good
			Cumene	good
40	Rigid to Flexible	Topas8007 ^(a) to Elvax CM576 ^(b)	Toluene	weak

5

Cyclohexanone	none
Methyl ethyl ketone	none
Methylene chloride	none
Tetrahydrofuran	none
Dimethyl formamide	none
Dimethyl sulfoxide	none

10

Rigid to Rigid	Topas 8007 ^(c) to Topas 8007 ^(c)	Cyclohexane	strong
		n-Butyl cyclo hexane	strong
		Xylene	strong
		Tetralin	strong
		Heptane	strong

15

Note:

(a) Injection molded into y-site.

(b) Extruded tubing.

(c) Compression molded sheet.

20

Bond strength was assessed by hand pull test , at one day after the solvent bonding.

Ratings:

None = Readily separable.

Weak = Some bond strength but easy to separate.

25 Good = Hard to separate, no material transfer is visible on the peeled surface but is suitable for providing a sterile, sturdy connection.

Strong = Very hard to separate, material transferring from one surface to another at the peeled bonding interface is visible.

30 V. Examples of cements made by dissolving the COC resin in solvents for bonding flexible polyolefin components:

The COC cements were prepared by dissolving the COC into a solvent at room temperature.

35 Elevated temperature such as 50°C can be used to enhance the speed of the preparation of the cement solution.

	<u>Cement formulation</u>	<u>Composition</u>	
40	A	coc resin: Topas 8007	1 %wt
		solvent: Cyclohexane	99%wt

	B	coc resin: Topas 8007	5 %wt
		solvent: Cyclohexane	95%wt
5	C	coc resin: Topas 8007	15%wt
		solvent: Cyclohexane	85%wt
	D	coc resin: Topas 8007	5 %wt
		solvent: n-Butyl cyclohexane	95%wt
10	E	coc resin: Topas 8007	5 %wt
		solvent: Decalin	95%wt
	F	coc resin: Topas 8007	5 %wt
		solvent: Heptane	95%wt
15	G	coc resin: Topas 5013	5 %wt
		solvent: Cyclohexane	95%wt
20	H	coc resin: Topas 5013	20 %wt
		solvent: Cyclohexane	80%wt

VI. Examples of bonding a flexible component to a flexible component using COC cement compositions of Example IV.

25 Tubings made of ULDPE (Engage 8003) or EVA (Elvax CM 576) were extruded and cut into segments. Cement was applied between bonding interfaces of the tubing segments identified in the following table. The bonding was done by applying small amount of the cement at the bonding interface. Bond strength was measured by a hand pull test conducted one day after bonding.

30	<u>Flexible to flexible bonding</u>	<u>Cement</u>	<u>Bond Strength</u>
	Engage 8003 to Engage 8003	A	weak
	Engage 8003 to Engage 8003	B	good
35	Engage 8003 to Engage 8003	C	good
	Engage 8003 to Engage 8003	D	good
40	Engage 8003 to Engage 8003	E	good
	Engage 8003 to Engage 8003	F	good

	Elvax CM 576 to Elvax CM 576	A	weak
	Elvax CM 576 to Elvax CM 576	B	good
5	Elvax CM 576 to Elvax CM 576	C	good
	Elvax CM 576 to Elvax CM 576	D	good
10	Elvax CM 576 to Elvax CM 576	E	good
	Elvax CM 576 to Elvax CM 576	F	good
	Elvax CM 576 to Elvax CM 576	G	good
15	Elvax CM 576 to Elvax CM 576	H	good

Bond strength was assessed by hand pull test, at one day after the bonding.

Ratings:

20 None = Readily separable.

Weak = Some bond strength but easy to separate.

Good = Hard to separate, no material transfer is visible on the peeled surface but is suitable for providing a sterile, sturdy connection.

25 Strong = Very hard to separate, material transferring from one surface to another at the peeled bonding interface is visible.

VI. COC Blends

30 Blends of the components set forth in the following table were prepared with a Brabender mixer at 250°C at 50 rpm for 4 minutes.

Films were prepared by compression molding at 450°F to a thickness about 0.4 mm.

The Haze property is useful for the end user to see through the medical device for the purpose of examining the liquid level, particulates, contamination, or the presence of drugs. Lower haze gives clearer view and higher haze gives a fuzzy view. Low haze is frequently a desirable property for medical devices such as solution containers, drug delivery devices, I.V. and blood sets, dialysis devices, and syringes.

35 The haze and total light transmittance of the film were measured using a ColorQuest instrument with both sides of the film wetted with isopropyl alcohol to remove the effect of surface roughness.

Example VI A: Blends of COC with styrenic copolymers and polypropylene.

		<u>Ratio (wt %)</u>	<u>Light Transmittance(%)</u>	<u>Haze(%)</u>
5	Topas 8007/Rexflex W304	30/70	70	85
		50/50	75	83
		70/30	75	81
10	Topas 8007/Kraton G1657	30/70	64	86
		50/50	82	80
		70/30	84	80
15	Topas 8007/K-Resin KR01	50/50	72	83
	Topas 6015/K-Resin KR01	50/50	58	86

Examples VI B-D: Blends of COC with polyethylene:

Summary:

The polymer blends that have lower haze, i.e. better clarity, are Topas 8007 blended with ethylene copolymers that have hexene comonomer polymerized with metallocene catalyst. The blends with the lowest haze are from the blends with polyethylene with hexene comonomer, polymerized with a metallocene catalyst and with a density of higher than 0.900 and more preferably higher than 0.93 (e.g. Marlex D350).

Example VI B: Blends of Topas 8007 (T_g ~ 80 deg C) and polyethylene with different comonomers.

	<u>COC Blend Composition</u>	<u>Blend Ratio</u>	<u>Comonomer in Polyethylene</u>	<u>Light Transmittance(%)</u>	<u>Haze(%)</u>
30	Topas 8007/Tafmer A4085	30/70	Butene	84	80
		50/50		89	70
		70/30		81	61
35	Topas 8007/Exact 3024	50/50	Butene	88	83
	Topas 8007/Exact 3128	50/50	Butene	88	77
	Topas 8007/Exact 4033	50/50	Butene	81	81
40	Topas 8007/Exact 3131	50/50	Hexene	93	60
	Topas 8007/Exact 3030	50/50	Hexene	84	64

5	Topas 8007/MarlexD143	30/70	Hexene	87	53
		50/50		91	58
		70/30		90	52
10	Topas 8007/MarlexD350	20/80	Hexene	89	54
		30/70		87	44
		50/50		91	46
		70/30		91	45
		90/10		92	25
15	Topas 8007/Affinity VP8770	50/50	Octene	85	72
	Topas 8007/Affinity PL1880	50/50		90	77
	Topas 8007/Engage 8411	50/50		91	84

20

Example VI C: Blends of Topas 6015 ($T_g \sim 160$ deg C) and polyethylene with different comonomers.

25	COC Blend Composition	Blend Ratio	Comonomer in Polyethylene	Light Transmittance(%)	Haze(%)
30	Topas 6015/Tafmer TFB-01	30/70	Butene	65	84
		50/50		78	85
		70/30		47	85
35	Topas 6015/MarlexD143	30/70	Hexene	76	85
		50/50		83	83
		70/30		77	79
40	Topas 6015/MarlexD350	30/70	Hexene	54	81
		50/50		80	72
		70/30		79	76
40	Topas 6015/Exact 3030	30/70	Hexene	86	84
		50/50		82	84
		70/30		62	83

Example VI D:

Blends of Topas 6017 (Tg~180 deg C), Topas 8007 (Tg ~ 80 deg C) and polyethylene with different comonomers.

5

Conclusion:

The blend that has reduced haze contains Topas 8007 and a metallocene catalyst polymerized ethylene-hexene copolymer.

10	COC Blend Composition	Blend	Comonomer	Light Transmittance(%)	Haze(%)
		Ratio	in Polyethylene		
15	Topas 6017/Topas 8007/Affinity VP8770	Octene			
		25/25/50		65	85
		30/20/50		69	85
20	Topas 6017/Topas 8007/Marlex D350	Hexene			
		15/15/70		91	69
		25/25/50		82	75
		35/35/30		89	42

It should be understood that any ranges or sets of ranges set forth herein includes any and all ranges, combination or subcombination of ranges therein.

While specific embodiments have been illustrated and described, numerous modifications are possible without departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

CLAIMS

1. A polymer composition comprising:
a first component obtained by copolymerizing a norbornene monomer and
5 an ethylene monomer, the first component being in an amount from about 1-99% by weight of the composition; and
a second component of an ethylene and α -olefin copolymer, the α -olefin having 6 carbons, the second component being in an amount from about 99% to about 1% by weight of the composition.
10
2. The composition of claim 1 wherein the first component has from about 20 to about 75 mole percent of the norbornene monomer.
3. The composition of claim 1 wherein the first component has from about
15 30 to about 60 mole percent norbornene monomer.
4. The composition of claim 3 wherein the glass transition temperature of the first component is from about 70°C to about 130°C.
- 20 5. The composition of claim 4 wherein the first component is present at least in an amount of about 30% by weight of the composition.
6. The composition of claim 1 wherein the second component is obtained using a metallocene catalyst.
25
7. The composition of claim 6 wherein the second component has a density from about 0.870 g/cc to about 0.960 g/cc.
8. The composition of claim 1 further comprising a third component of a
30 homopolymer or copolymer obtained using a monomer selected from the group of a cyclic olefin or a bridged polycyclic hydrocarbon.
9. The composition of claim 5 wherein the third component is a second norbornene and ethylene copolymer different from the first component.

10. The composition of claim 9 wherein the third component has a glass transition temperature higher than about 120°C and the first component has a glass transition temperature lower than about 120°C.

5 11. The composition of claim 9 wherein the third component is present in an amount from 10% to about 90% by weight of the composition.

12. The composition of claim 11 wherein the first component and second component are present in a ratio of from about 2:1 to about 1:2 by weight.

10

13. A medical device fabricated from of any of the compositions set forth in claims 1-12.

14. A method for using a polymeric cement to assemble medical devices
15 comprising the steps of:

providing a first article of a low crystallinity polymer;
providing a second article of a low crystallinity polymer;
providing a cement composition having a first component of a cyclic olefin containing polymer or a bridged polycyclic hydrocarbon containing polymer and
20 a second component of an effective amount of a hydrocarbon solvent having a solubility parameter of less than about 20 (MPa)^{1/2} and a molecular weight of less than about 200 g/mole;

applying the cement composition to one of the first and second articles to define a bonding area; and

25 attaching the first article to the second article along the bonding area to fixedly attach the first article to the second article.

15. The method of claim 14 wherein the low crystallinity polymers is selected from the group comprising COCs, COC blends having minimally 30% COC by weight,
30 polymethyl pentene, polyolefins having a modulus of elasticity of less than 10,000 psi when measured in accordance with ASTM D790, and styrene containing polymers without modulus limitations.

16. The method of claim 15 wherein the low crystallinity polymer is a homopolymer or copolymer of polyethylene.

17. The method of claim 16 wherein the copolymers of ethylene are selected from the group comprising (a) ethylene copolymerized with monomers selected from the group of α -olefins having 3-10 carbons, lower alkyl and lower alkene substituted carboxylic acids and ester and anhydride derivatives thereof, (b) ethylene-propylene rubbers, (c) EPDM, and (d) ionomers.

18. The method of claim 14 wherein the cyclic hydrocarbons have from 5 to about 10 carbons in the ring.

19. The method of claim 18 wherein the cyclic hydrocarbons are selected from the group consisting of substituted and unsubstituted cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene.

20. The method of claim 14 wherein the bridged polycyclic hydrocarbon has at least 7 carbons.

21. The method of claim 20 wherein the bridged polycyclic hydrocarbons have at least two rings.

22. The method of claim 21 wherein the bridged polycyclic hydrocarbon is norbornene.

23. The method of claim 14 wherein the first component is obtained by copolymerizing the cyclic hydrocarbon or the bridged polycyclic hydrocarbon with a comonomer.

24. The method of claim 23 wherein the comonomer is selected from the group comprising α -olefins having from 2-10 carbons, aromatic hydrocarbons, cyclic hydrocarbons, and bridged polycyclic hydrocarbons.

25. The method of claim 24 wherein the first component is a copolymer of a norbornene monomer and an ethylene monomer.

26. The method of claim 25 wherein the norbornene monomer is present in
5 at least about 20 mole percent of the copolymer.

27. The method of claim 26 wherein the norbornene is present from about 30 to about 60 mole percent.

10 28. The method of claim 27 wherein the glass transition temperature of the first component is from about 70°C to about 180°C.

29. The method of claim 14 wherein the cement composition has a third component of a polymer selected from the group consisting of polyethylene copolymers
15 having a density less than 0.880 g/cc, polymethyl pentene, polypropylene having a modulus of less than 10,000 psi, styrene containing copolymers and styrene containing interpolymers.

30. The method of claim 29 wherein the first component of the cement is a
20 copolymer of norbornene and ethylene.

31. The method of claim 30 wherein the third component is an ethylene and α -olefin copolymer.

25 32. The method of claim 14 wherein the first component is present in an amount of from about 1-20% by weight of the cement composition.

33. The method of claim 14 wherein the first component is present in an amount of from about 1-15% by weight of the cement composition.

30

34. The method of claim 14 wherein the first component is present in an amount of from about 3-15% by weight of the cement composition.

35. The method of claim 30 wherein the first article and the second article are flexible.

36. The method of claim 14 wherein the first article is a medical tubing of an ethylene and α -olefin copolymer or an ethylene vinyl acetate copolymer or an ethylene methacrylate copolymer and the second article is a medical housing.

37. The method of claim 36 wherein the medical housing has a modulus of elasticity of greater than about 30,000 psi as measured in accordance with ASTM D790.

10

38. The method of claim 37 wherein the medical housing is of a polymeric material selected from the group of cyclic hydrocarbon containing polymers and bridged polycyclic hydrocarbon containing polymers.

15

39. A medical device assembled using any of the methods of claims 14-38.

40. A method for assembling a medical device using solvent bonding techniques comprising the steps of:

20

providing a first article of a polymer composition comprising a first component of a homopolymer or copolymer obtained using monomers of cyclic olefin or a bridged polycyclic hydrocarbon, the first component being present in an amount from about 30% to about 100% by weight of the composition and a second component from 0-70% by weight of the composition;

25

providing a second article of a material selected from the group comprising low crystallinity polymers;

applying a solvent to one of the first article or the second article to define an interface area; and

bonding the first article to the second article along the interface area.

30

41. The method of claim 40 wherein the cyclic olefins have from 5 to about 10 carbons in the ring.

42. The method of claim 41 wherein the cyclic olefins are selected from the group consisting of substituted and unsubstituted cyclopentene, cyclopentadiene,

cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene,

43. The method of claim 40 wherein the bridged polycyclic hydrocarbon has
5 at least 7 carbons.

44. The method of claim 43 wherein the bridged polycyclic hydrocarbons are selected from the group consisting of polycyclic hydrocarbons having at least 7 carbons.

10 45. The method of claim 44 wherein the bridged polycyclic hydrocarbon is norbornene.

46. The method of claim 40 wherein the first component is obtained by copolymerizing the cyclic olefin or the bridged polycyclic hydrocarbon with a
15 comonomer.

47. The method of claim 46 wherein the comonomer is selected from the group comprising α -olefins having from 2-10 carbons, aromatic hydrocarbons, cyclic olefins, and bridged polycyclic hydrocarbons.
20

48. The method of claim 47 wherein the first component is a copolymer of a norbornene monomer and an ethylene monomer.

49. The method of claim 48 wherein the norbornene monomer is present in
25 at least about 20 mole percent of the copolymer.

50. The method of claim 49 wherein the norbornene is present from about 30 to about 60 mole percent.

30 51. The method of claim 50 wherein the glass transition temperature of the first component is from about 70°C to about 180°C.

52. The method of claim 40 wherein the first article has a second component of a polymer selected from the group consisting of homopolymers and copolymers of ethylene, propylene, butene, hexene, octene, nonene, decene and styrene.
- 5 53. The method of claim 52 wherein the second component is an ethylene and α -olefin copolymer.
54. The method of claim 53 wherein the low crystallinity polymer is selected from the group comprising COCs, COC blends having minimally 30% COC by weight,
10 polymethyl pentene, polyolefins having a modulus of elasticity of less than 10,000 psi when measured in accordance with ASTM D790, and styrene containing polymers without modulus limitations.
55. The method of claim 54 wherein the low crystallinity polymer is a
15 homopolymer or copolymer of polyethylene.
56. The method of claim 55 wherein the copolymers of ethylene are selected from the group comprising (a) ethylene copolymerized with monomers selected from the group of α -olefins having 3-10 carbons, lower alkyl and lower alkene substituted
20 carboxylic acids and ester and anhydride derivatives thereof, (b) ethylene-propylene rubbers, (c) EPDM, and (d) ionomers.
57. The method of claim 56 wherein the second article is selected from an ultra
25 low density polyethylene and ethylene and vinyl acetate copolymer.
58. The method of claim 57 wherein the ultra low density polyethylene is obtained using a metallocene catalyst.
59. The method of claim 57 wherein the ethylene vinyl acetate copolymer has a
30 vinyl acetate content from 5% to about 32%.
60. The method of claim 40 wherein the second article is of an ultra low density polyethylene.

61. The method of claim 40 wherein the second article is of an ethylene and vinyl acetate copolymer.

62. The method of claim 40 wherein the second article is of a material
5 selected from the group of rigid, semi-rigid and flexible polymers.

63. The method of claim 53 further comprising a third component of a homopolymer or copolymer obtained using a monomer selected from the group of cyclic olefins or a bridged polycyclic hydrocarbons.

10 64. The method of claim 63 wherein the first component has a glass transition temperature of lower than 120°C and the third component has a glass transition temperature higher than about 120°C.

15 65. The method of claim 64 wherein the third component is present in an amount from 10% to about 90% by weight of the composition.

66. The method of claim 65 wherein the first component and second component are present in a ratio of from about 2:1 to about 1:2 by weight.

20 67. The method of claim 66 wherein the first article is a medical housing.

68. The method of claim 67 wherein the second article is a medical tubing of a polyolefin.

25 69. The method of claim 40 wherein the solvent has a solubility parameter of less than 20 (MPa)^{1/2} and having a molecular weight less than about 200 g/mole.

70. The method of claim 69 wherein the solvent is selected from the group of
30 aliphatic hydrocarbons, aromatic hydrocarbons, mixtures of aliphatic hydrocarbons, mixtures of aromatic hydrocarbons and mixtures of aromatic and aliphatic hydrocarbons.

71. The method of claim 70 wherein the aliphatic hydrocarbon is selected from the group consisting of substituted and unsubstituted hexane, heptane, cyclohexane, cycloheptane, and decalin
- 5 72. The method of claim 70 wherein the aromatic hydrocarbon is selected from the group consisting of substituted and unsubstituted xylene, tetralin, toluene, and cumene.

FIG. 1

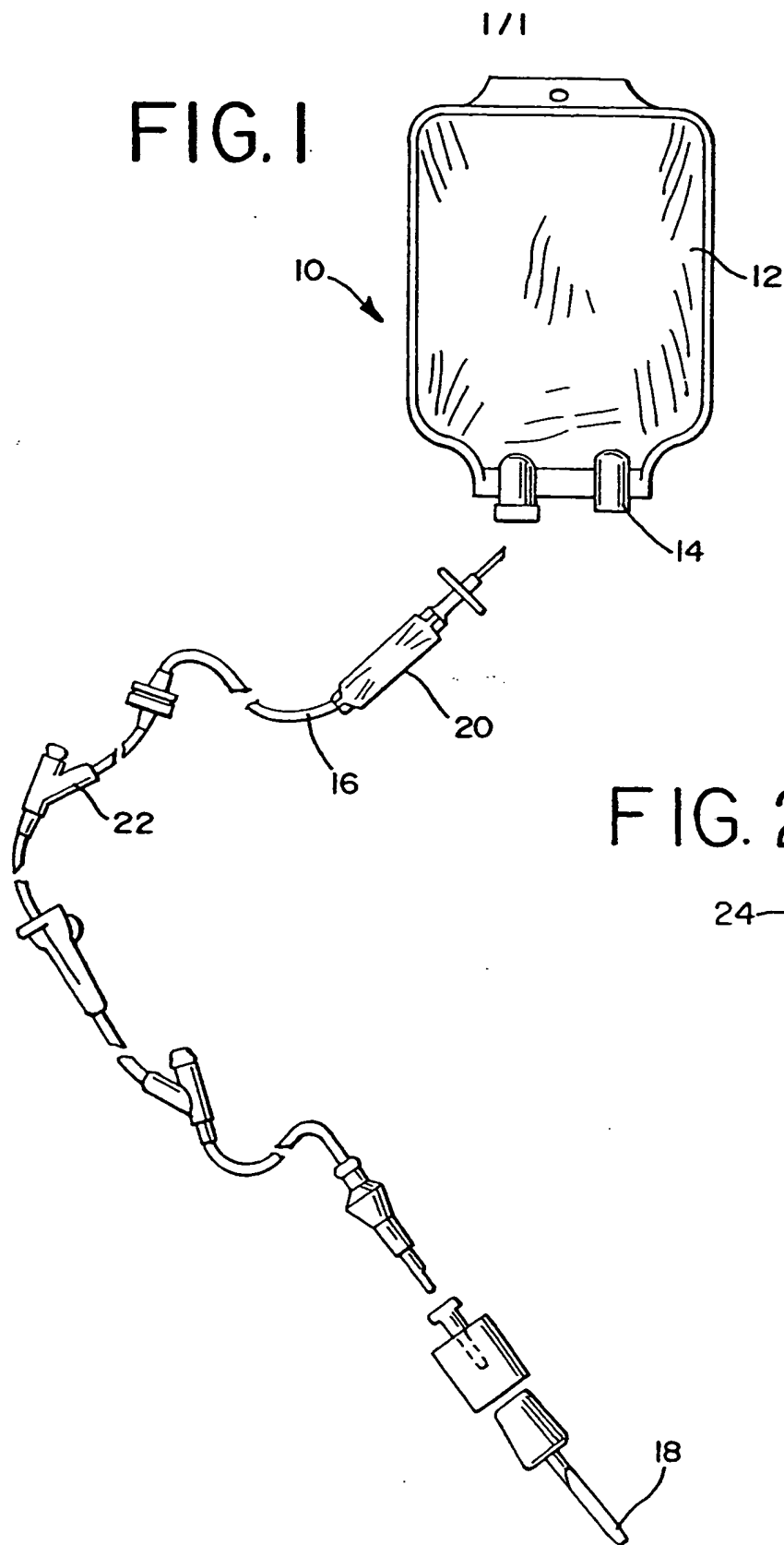
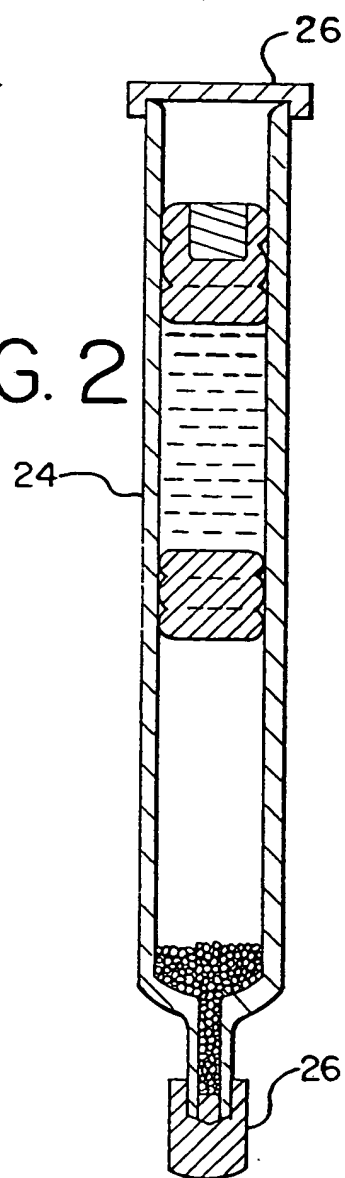


FIG. 2



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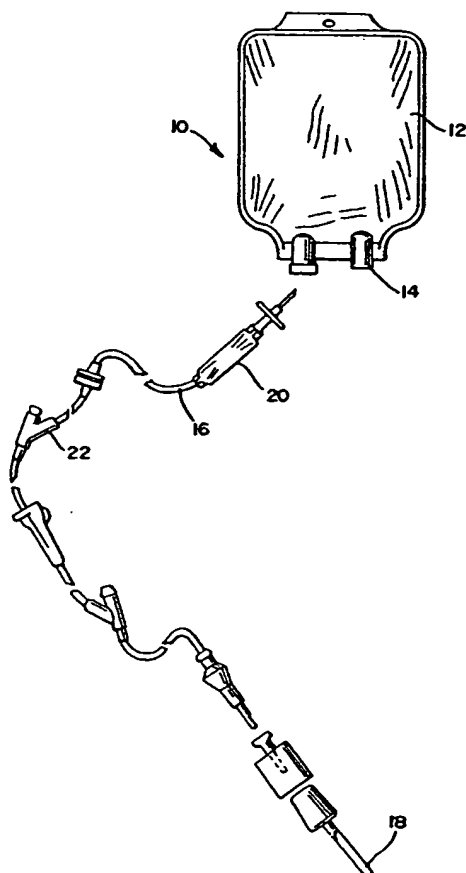
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[Continued on next page]

(54) Title: CYCLOOLEFIN BLENDS AND METHOD FOR SOLVENT BONDING POLYOLEFINS



(57) Abstract: The present invention provides a polymer composition having a first component obtained by copolymerizing a norbornene monomer and an ethylene monomer, the first component being in an amount from about 1-99 % by weight of the composition; and a second component of an ethylene and α -olefin copolymer, the α -olefin having 6 carbons, the second component being in an amount from about 99 % to about 1 % by weight of the composition.

WO 01/18112 A3



HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 44043 A (EXXON CHEMICAL PATENTS INC) 8 October 1998 (1998-10-08) claims; examples; table 1 ---	1,2,4-7, 13
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 275 (C-0849), 12 July 1991 (1991-07-12) & JP 03 095286 A (MITSUI PETROCHEM IND LTD), 19 April 1991 (1991-04-19) abstract ---	14,20-26
P,X	WO 99 48990 A (KODEMURA JUNJI ;NIPPON ZEON CO (JP); SAKAMOTO MASATO (JP)) 30 September 1999 (1999-09-30) claim 12 --- -/--	14,20-22

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 058 (C-1159), 31 January 1994 (1994-01-31) & JP 05 277154 A (IDEMITSU KOSAN CO LTD), 26 October 1993 (1993-10-26) abstract ---	40
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 071554 A (YOKOHAMA RUBBER CO LTD;THE;NIPPON ZEON CO LTD), 16 March 1999 (1999-03-16) abstract -----	40

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/24710

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 9-12
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 00/24710

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box 1.2

Claims Nos.: 9-12

Present claims 9-12 relate to a product by reference to the "third component as defined in claim 5"; whereby claim 5 is not defining any third component.

The use of this formulation in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the wording the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 00/24710

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-13

A polymer-composition comprising cycloolefine-copolymer and ethene-hexene-copolymer

2. Claims: 14-39

A method of bonding two polymeric articles by applying a solution of a cycloolefinic copolymer at the bonding area

3. Claims: 40-72

Method of bonding by the solvent method, characterised that at least one of the articles to be bonded is formed by a cycloolefine copolymer

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC, US 00/24710

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JP 05277154 A	26-10-1993	NONE	
JP 11071554 A	16-03-1999	NONE	